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FORMATION OF PYROPHORIC FRAGMENTS

Warren W. Hillstrom

Ballistic Research Laboratories
Aberdeen Proving Ground, Maryland

June 1973

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MEMORANDUM REPORT NO. 2306

(Supersedes IMR No. 46)

FORMATION OF PYROPHORIC FRAGMENTS

by

Warren W. Hillstrom

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AD 765447

34

Unclassified
Security Classification

DOCUMENT CONTROL DATA - R & D		
(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)		
1. ORIGINATING ACTIVITY (Corporate number) USA Ballistic Research Laboratories Aberdeen Proving Ground, Md. 21005		20. REPORT SECURITY CLASSIFICATION Unclassified
		21. GROUP
2. REPORT TITLE Formation of Pyrophoric Fragments		
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) BRL Report June 1971 - December 1972		
5. AUTHOR(S) (First name, middle initial, last name) Warren W. Hillstrom		
6. REPORT DATE JUNE 1973	7a. TOTAL NO. OF PAGES 39	7b. NO. OF REFS 11
8a. CONTRACT OR GRANT NO. N/A	8b. ORIGINATOR'S REPORT NUMBER(S) BRL MEMORANDUM REPORT NO. 2306	
9. PROJECT NO. RDT&E 1T061102A33E		
c.	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
d.		
10. DISTRIBUTION STATEMENT This document has been approved for public release and sale; its distribution is unlimited.		
11. SUPPLEMENTARY NOTES Supercedes IMR No. 46	12. SPONSORING MILITARY ACTIVITY US Army Materiel Command 5001 Eisenhower Avenue Alexandria, Virginia 2304	
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14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Pyrophoric Metals Incendiaries Metal combustion Reactive fragments misch metal zirconium titanium						

Unclassified

Security Classification

BALLISTIC RESEARCH LABORATORIES

MEMORANDUM REPORT NO. 2306

/ (Supersedes IMR No. 46)

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FORMATION OF PYROPHORIC FRAGMENTS

Warren W. Hillstrom

Terminal Ballistics Laboratory

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Whillstrom/mba/2632
Aberdeen Proving Ground, Md.
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FORMATION OF PYROPHORIC FRAGMENTS

ABSTRACT

An empirical correlation was developed to predict pyrophoric sparking from two properties: (1) the standard free energy of formation per oxygen atom in the metal oxide and (2) the metal oxide volume compared with metal volume.

The ignition of pyrophoric metals is usually studied with very small particle sizes resulting in very large surface effects. A simple impact test was developed to study large pyrophoric pellets and the formation of free flying fragments in the laboratory. This paper describes the test and reports test results for cerium, misch metal, zirconium, and titanium. Each of the metals exhibited different threshold conditions for initiation of pyrophoric sparking. An experimental criterion was defined as the Lower Glow Temperature.

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1. INTRODUCTION

Pyrophoric materials are defined by Webster as those that (1) ignite spontaneously and/or (2) emit sparks when scratched or struck. Many materials ignite spontaneously in oxidizing atmospheres as a result of their extreme reactivity. Examples of such materials are metal hydrides and alkyls such as lithium hydride and trimethyl aluminum. Dusts of very small diameter metal particles may also ignite when exposed to air at room temperature. The ignition temperatures of these dusts usually vary with particle size and surface history.^{1*,2,3}

In this exploratory study, we are concerned primarily with the second definition where bulk metal pieces spark profusely when ground, abraded, impacted, or otherwise subjected to mechanical shock. Pyrophoric sparking is a unique, little understood property of a few metals. It is the purpose of this work to investigate the nature of pyrophoricity and furnish a method for distinguishing between materials that are pyrophoric and others that are not. Both empirical correlations of the available physical properties of the elements and an experimental test of pyrophoric sparking were employed toward this end.

Cerium, zirconium and uranium are most commonly described as pyrophoric metals in terms of the above definition. Some of the chemical and physical properties of these metals are shown in Table I. Cerium is the major constituent of misch metal which is used in the manufacture of lighter flints. The ease of sparking of lighter flints is well known. The character of the sparks from present day lighter flints is somewhat different from the old flint and steel sparks. The former ignite hydrocarbon fuel-air mixtures while the old flint and steel sparks could only ignite extremely flammable material such as tinder or charred cloth. Sparks from pyrophoric materials sometimes multiply in dramatic cascades.

As shown in Table I, uranium has a relatively low spontaneous ignition temperature. When such temperatures are reported, they have

References are listed on page 35.

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been measured for powders. The results are seen to vary greatly with particle size, surface oxidation, and surface history, such as annealing and the presence or lack of chemically or physically absorbed films.^{9,10}

Table I. Properties of Pyrophoric Metals

	<u>Zr</u>	<u>Ce</u>	<u>U</u>
Atomic Number ⁴	40	58	92
Electronic Structures ⁵	4d ² 5s ²	4f ¹ 5d ¹ 6s ²	5f ³ 6d ¹ 7s ²
Specific Gravity (20°C)	6.506	6.771	18.95
M.P., °C ⁴	1852	798	1132
B.P., °C ⁴	4377	3257	3818
Heat of Comb., K cal/g ⁶	2.8	1.9	1.09 ⁷
Heat of Comb., K cal/cm ³⁶	18	13	20.4 ⁷
Spontaneous Ignition Temperature, °C ⁸	150	150-180	20

The surface area available for reaction is increased greatly by subdivision of a given mass of material. For example, the surface area on one gram of a material with a density of 2.30 is shown in Table II for subdivision in cubes with an edge length, ℓ .

Table II. Effect of Particle Size on Surface Area¹¹

ℓ , cm	A , cm ² /g
10 ⁻¹	26.1
10 ⁻³	261.0
10 ⁻⁵	261,000
10 ⁻⁶	2,610,000
10 ⁻⁷	26,100,000

Normally, high surface area to mass ratios greatly magnify solid surface effects in reactions with gases. Thus, experiments involving ignition of powders require careful attention to experimental conditions and

metal surface history for meaningful, consistent results.

The electronic structure of these pyrophoric metals disclose two common characteristics. They are transition metals and all three have largely unfilled d shells. Cerium has $5d^1$; uranium has $5d^1$ and zirconium has $4d^2$. Thus, large numbers of orbitals are available for coordination and reaction. This is in contrast to the comparatively stable transition metal, tungsten, which has $5d^4$.

Up to now, field tests have been used widely to evaluate the effectiveness of munitions containing pyrophoric metals against a variety of combustible fuel targets. However, many loosely controlled factors significantly affect these tests, often leading to inconsistent and questionable results. Some of these variable factors include temperature, contamination, and evaporation of the fuel along with the general target geometry and environment. Adequate control of all of these factors is a difficult and continuing task.

On the other hand, a laboratory test has the advantage of generally better controlled test conditions, lower manpower and cost requirements, and quick response. It would be most useful as a screening test to determine the sparking ability of different materials. The test could then furnish a means to study the formation of pyrophoric fragments and their efficiency as an ignition source. Field tests should also be carried out to assess the efficiency of materials proved effective in the screening test.

II. EMPIRICAL TREATMENT OF PROPERTIES

Since an intuitive examination of metal sparking indicated that some physical and chemical properties might correlate with the degree of pyrophoricity, the known properties of some pyrophoric metals were compared with those of non-pyrophoric metals. No obvious relationship was found between thermal conductivity and pyrophoricity. Properties that do correlate are (1) the reactivity of the metal with oxygen or air, and (2) oxide volume compared with metal volume. The standard free

energy of formation per oxygen atom in the metal oxide is a parameter indicating relative metal reactivity with oxygen. It is also a good indicator of the heat available from reaction of the metal with oxygen.

The other parameter of interest is oxide expansion. The violent expansion of metal during its oxidation may be one cause of the explosive cascading, or "popcorning," observed with pyrophoric sparks. To explore this concept the ratios of the metal oxide and metal specific volumes were calculated by means of the following formula:

$$\frac{\frac{F_o}{D_o}}{\frac{A_m}{D_m}} = \frac{F_o D_m}{A_m D_o}$$

where

F_o = formula weight of oxide/atom of metal

D_m = metal density

A_m = atomic weight of the metal

D_o = metal oxide density.

For example, the ratio of oxide to metal for titanium is

$$\frac{(72.9)}{(47.9)} \frac{(4.50)}{(4.26)} = 1.76$$

Comparison of this ratio with those for other metals gives a relative order of magnitude for the expansion of the reacting material. A correlation of this ratio and the free energy of formation of the oxide for 15 elements is shown in Figure 1.

It can be seen that these measures of reactivity and oxide expansion allow a general separation of known pyrophoric and nonpyrophoric elements. Uranium, cerium and zirconium have both relatively high reactivity and oxide volume ratio. Aluminum is an exception. Its dust ignites easily.

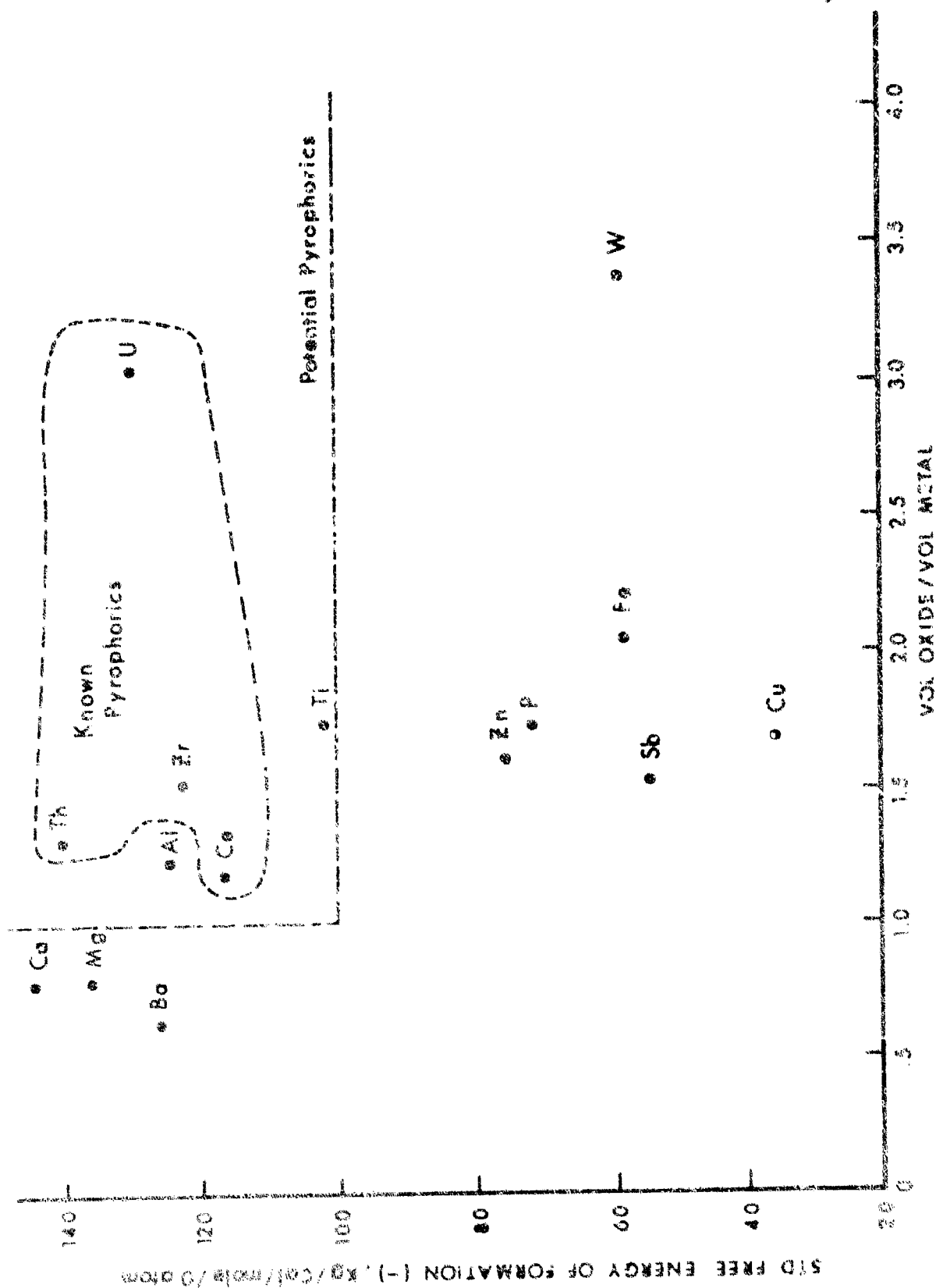


Figure 1 -- Free Energy of Formation vs Oxide Expansion

but the pure metal is apparently too soft to spark appreciably when abraded. Thus, if other anomalies are found some additional metal property such as hardness may have to be considered to estimate pyrophoricity. Thorium also has relatively high reactivity and a high oxide volume ratio. It has been called pyrophoric⁹, but its sparking ability should be investigated further in the tests described in this report.

From this correlation, empirical criteria for pyrophoricity were tentatively established to determine promising pyrophoric materials. The threshold for negative standard free energy of formation was set at 100 since titanium is 101.9 kg cal/mole/o atom. Titanium in experiments to be described later shows a tendency to spark profusely upon impact. The other parameter of interest in the above correlation is the ratio of specific volumes of oxide/metal. From the sharp division of pyrophoric and non-pyrophoric in the correlation, a specific volume ratio of 1.0 was selected as the threshold. It appears necessary for a metal to have values above both threshold criteria in order to be pyrophoric.

Sufficient data were available for 60 elements to estimate their pyrophoricity according to these criteria. Some 14 elements possess properties that suggest pyrophoric behavior. The results are summarized in Table III. The elements that fit this pyrophoricity criteria are: aluminum, beryllium, cerium, hafnium, lanthanum, neodymium, plutonium, praseodymium, samarium, thorium, titanium, uranium, yttrium, and zirconium. These materials should be tested further to confirm their pyrophoric tendencies. Alloys of pyrophoric with other pyrophoric and pyrophoric with non-pyrophoric materials could also be considered. For example, both ZrSn and FeCe alloys spark profusely under impact.⁶

TABLE III
Empirical Pyrophoricity Determination

Oxide	ΔF_f^o Kg Cal/mole/o	Vol. Oxide Vol. Element	Estimated Pyrophoricity
Al ₂ O ₃	-125.59	1.28	Yes
As ₄ O ₆	- 45.89	2.02	No
Sb ₂ O ₄	- 47	1.44	No
BaO	-126.3	.78	No
BeO	-139.0	2.77	Yes
Bi ₂ O ₃	- 39.57	1.28	No
Br ₂ O ₃	- 94.33	3.06	No
CaO	- 53.79	1.21	No
CaO	-144.4	.83	No
CeO ₂	-116*	1.23	Yes
Cs ₂ O	- 75.9*	0.468	No
Cr ₂ O ₃	- 83.6	3.92	No
CoO	- 51.0	2.10	No
Cu ₂ O	- 34.94	1.70	No
Ga ₂ O ₃	- 86*	1.350	No
GeO ₂	- 64.1*	1.23	No
Au ₂ O ₃	+ 13.6	-	No
HfO ₂	-135.7*	1.62	Yes
In ₂ O ₃	- 74.2*	1.22	No
IrO ₂	- 20.1*	8.30	No
Fe ₂ O ₃	- 59.0	2.06	No
La ₂ O ₃	-153*	1.11	Yes
PbO ₂	- 26.17	1.31	No
Li ₂ O	-142.4*	.60	No
MgO	-136.13	0.84	No
MnO ₂	- 55.7	2.07	No
HgO	- 13.99	1.32	No
MoO ₃	- 53.98	3.25	No
Nd ₂ O ₃	-147.3*	1.12	Yes
NiO	- 51.7	1.68	No
Nb ₂ O ₅	- 92.6*	2.74	No

TABLE III

Empirical Pyrophoricity Determination (continued)

Oxide	ΔF_f^0	Vol. Oxide	Estimated
	Kg Cal/mole/o	Vol. Element	Pyrophoricity
OsO ₄	- 17.6	6.12	No
F ₂ O	- 20.4*	1.51	No
P ₄ O ₁₀	- 72.0**	1.75	No
PuO ₂	-126*	1.96	Yes
PoO ₂	- 23.1	-	No
K ₂ O	- 86.4*	0.51	No
Pr ₂ O ₃	-148.2*	1.12	Yes
RaO	-125*	-	-
Re ₂ O ₇	- 42.5*	4.38	No
Rh ₂ O ₃	- 22.8*	2.29	No
Rb ₂ O ₂	- 50.9*	0.498	No
RuO ₂	- 26.3*	2.32	No
SeO ₂	- 27.5	1.71	No
SiO ₂	- 96.2	2.04	No
Ag ₂ O	- 2.59	1.58	No
Na ₂ O	- 90.0	0.32	No
Sm ₂ O ₃	- 103	1.06	Yes
SrO	- 133.8	0.69	No
Ta ₂ O ₅	- 94.1	2.47	No
TeO ₂	- 32.3	1.38	No
Tl ₂ O	- 32.5	1.29	No
ThO ₂	-140.1***	1.36	Yes
SnO ₂	- 62.1	1.19	No
TiO ₂	-101.9	1.78	Yes
WO ₃	- 60.8	3.40	No
UO ₂	-128	3.10	Yes
V ₂ O ₅	- 68.8	3.17	No
Y ₂ O ₃	-102	1.44	Yes
ZnO	- 76.05	1.63	No
ZrO ₂	-122.2	1.55	Yes

*Calculated from ΔH_f^0 **Calculated from ΔH_f^0 in Handbook of Chemistry, N. Lange, Ed., 9 Ed., 1956.***Calculated from ΔF_f^0 in Handbook of Chemistry, N. Lange Ed., 9 Ed., 1956.

III. EXPERIMENTAL

Metal samples were used as obtained from the suppliers. Sponge (irregular, fractured lumps), solid rod, and dust samples of zirconium as Commercial Grade 11 were supplied by Amax Specialty Metals, Inc., Akron, New York. Lengths of 3/16" diameter misch metal rod were purchased from Ronson Metals Corporation, Newark, N.J. Both 75M2 (75% rare earths, 23% iron, 2% magnesium) and 95M (95% rare earths, 5% magnesium) grades were used. A typical analysis of the rare earths in misch metal is 53% cerium, 24% lanthanum, 16% neodymium, 5% praseodymium, 2% other rare earths. Pure cerium (99.9%) ingots were purchased from Research Organic/Inorganic Chemical Corp., Sun Valley, Calif. and carefully machined to the desired shapes. Lump, reagent grade antimony was obtained from Fisher Scientific Co., Pittsburgh, Pa. Pure aluminum and copper rods were obtained locally. Irregular lumps of titanium metal were purchased from Fisher Scientific Company as fused titanium metal, C.P.

IV. METAL TEMPERATURE EFFECTS

A. Misch Metal and Cerium

In order to test the ignition of metal samples larger than dusts, metal samples ranging in weight from a few milligrams to several grams were heated to temperatures at and above their reported "autoignition temperatures." For example, 75M2 misch metal was heated at 200° in air for 3 days without glowing, burning, or sparking. It only corroded or oxidized slower. This is in contrast to its reported autoignition temperature of 150-180°C. When the misch metal was heated at higher temperatures (600-1000°C) in air it glowed bright orange, but still no flames, sparks, or burning were seen. In an argon atmosphere the misch metal did not glow brightly when heated at 830°C. The same piece glowed brightly when subsequently exposed to air. Thus, the glowing apparently results from an oxidation reaction.

This bright orange glow was necessary for profuse sparks upon impact with drop weights as will be discussed later in this report. An iron nut in the furnace served as a reference for the appearance of glowing although the pyrophoric glowing was bright enough itself to be easily distinguished from normal radiation.

Bulk pieces above the Lower Glow Temperature begin to glow at lengths of time dependent on the furnace temperature. The length of time was measured from the beginning of heating until the appearance of the bright orange glow. Figure 2 shows the time to glow as a function of furnace temperature. Small rods of 75M2 misch metal, 3/16" diameter by 1/2" length, were set in a combustion boat in the hot furnace and the time measured for the onset of a bright orange glow. At temperatures below about 400°C no bright orange glow appeared. This limiting temperature is the Lower Glow Temperature. Bulk pieces do not glow at temperatures below the Lower Glow Temperature.

The time to glow for 95M misch metal is shown in Figure 3. Shorter times to the beginning of bright glowing were observed, but the Lower Glow Temperature Limit is about the same as that found for 75M2 within the experimental error.

Pure cerium pellets with the same geometry began to glow faster than 75M2 and 95M. For example, at 600°C it began to glow in only 27 seconds compared with 98 seconds for 75M2 and 50 seconds for 95M.

B. Zirconium

Zirconium sponge was heated similarly, but the time to glow was very dependent on particle size as shown in Figure 4. As might be expected, the smaller particles begin to glow in a much shorter time than larger pieces exposed to the same temperatures. This may be due to heat loss from the metal particle surface to the interior. This would result from heat transfer losses to the interior of the metal particle from the surface. The oxidation appears to proceed in two steps, giving an orange glow first, and then white incandescence for particles ranging from 0.18 g up to a gram. Since the white incandescent state was needed for sparks on impact

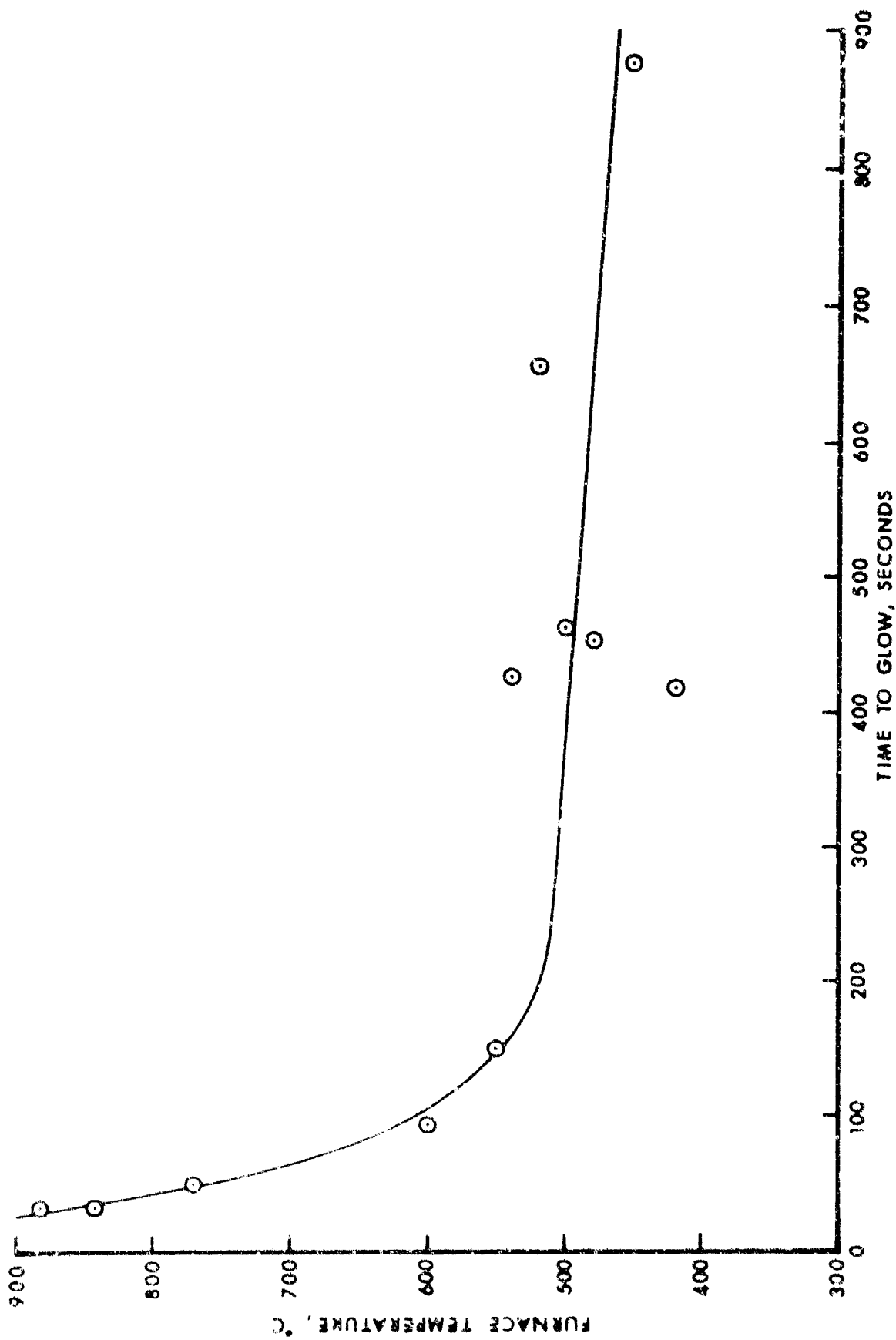


Figure 2 - 75M2 Misch Metal Temperature vs. Glow Time

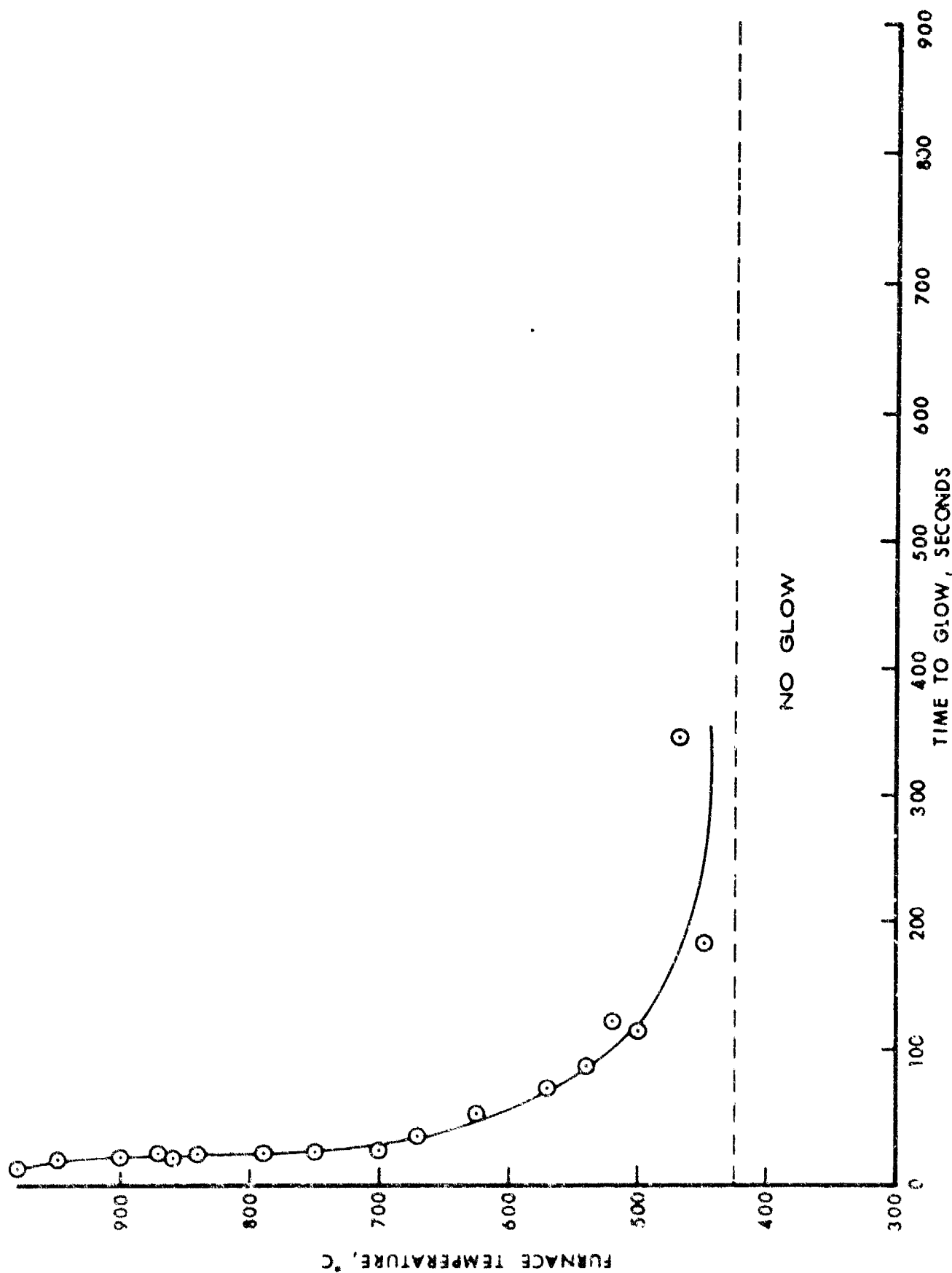


Figure 3 — 95M Misch Metal Temperature vs Glow Time

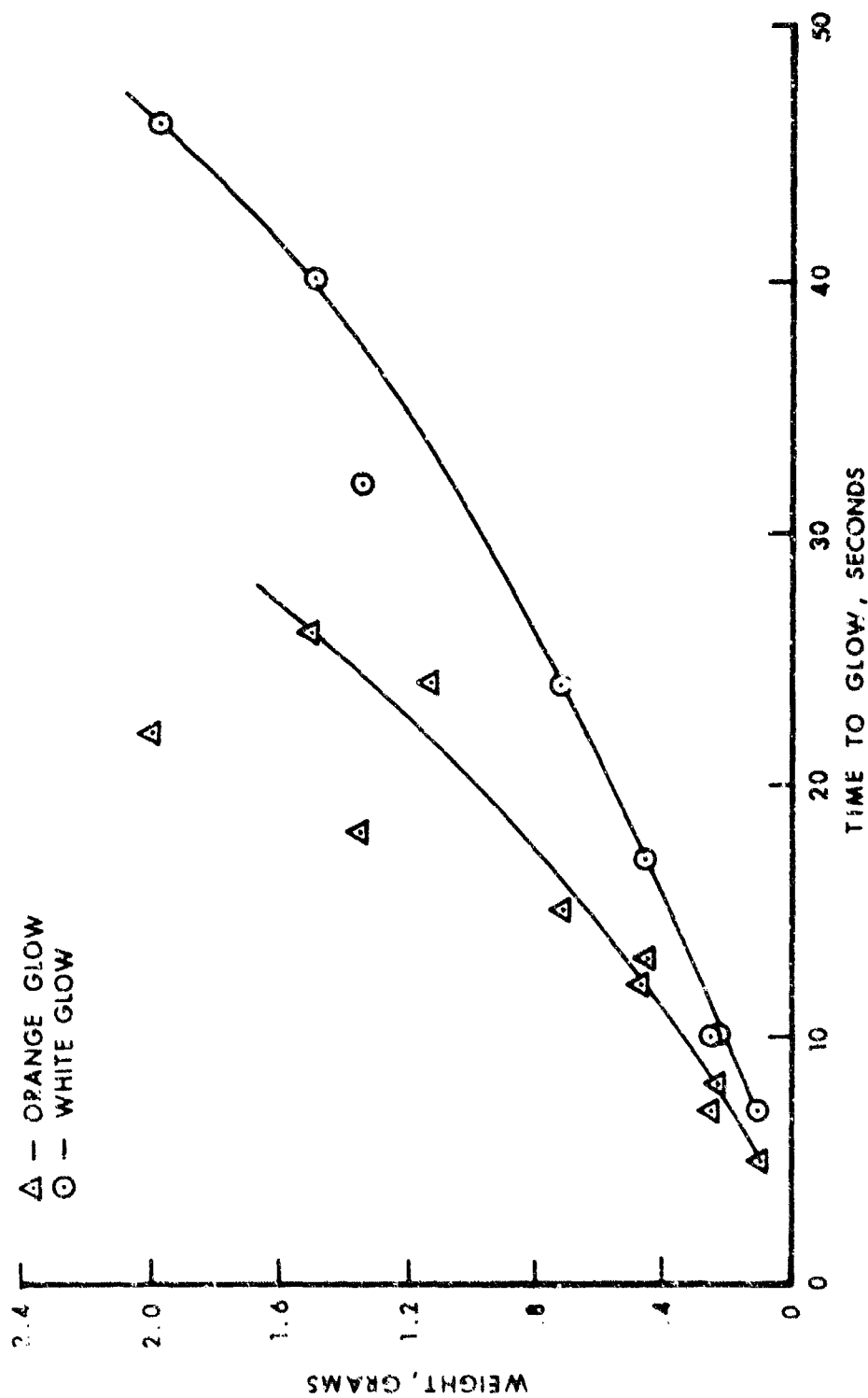


Figure 4 - Zirconium, 740 °C

(with zirconium no sparks could be initiated by impact during the orange glowing phase) the Lower Glow Temperature was 580°C .

The time to glow for zirconium sponge as a function of furnace temperature is shown in Figure 5. Three particles of $0.80 \pm .06$ g were used in this case. Larger pieces had a much flatter curve with much longer times to glow. Smaller pieces showed little variation in time to glow with furnace temperatures, but were either "glow or no-glow" at temperatures above or below 580°C , respectively.

Pieces of solid zirconium rod in the same weight range showed dissimilar behavior in that they only glowed orange. They did not progress to the white incandescent state after heating at 900°C for periods up to 12 minutes. The reasons for this difference in behavior are not well understood. Further work with different physical forms of zirconium may be needed to clarify their behavior. Void spaces in the sponge may act as insulation and prevent heat loss during rapid oxidation of the metal since the specific gravity of the zirconium sponge used in these experiments was measured to vary from 2.4 to 22.9% lower than the literature value.

C. Titanium

Titanium behaved like zirconium as shown in Figure 6 (920°C) and 7 (870°C). Samples of sponge titanium proceeded through an orange glow to white incandescence. The pieces did not always proceed to whiteness. At lower temperatures, even after ten minutes heating, no samples would go to whiteness. Since the whiteness was needed for sparks on impact, the Lower Glow Temperature for titanium sponge appears to be 870°C . As with zirconium, solid titanium rod would not go to whiteness after heating at 900°C for long periods.

D. Other Metals

Some metals that are not predicted to be pyrophoric were also heated. Aluminum only melted when its temperature rose to the melting point (660°C) without any sign of glowing, sparking, or burning. Antimony (m.p. 630°C) behaved similarly. Copper (m.p. 1083°C) did not glow, spark,

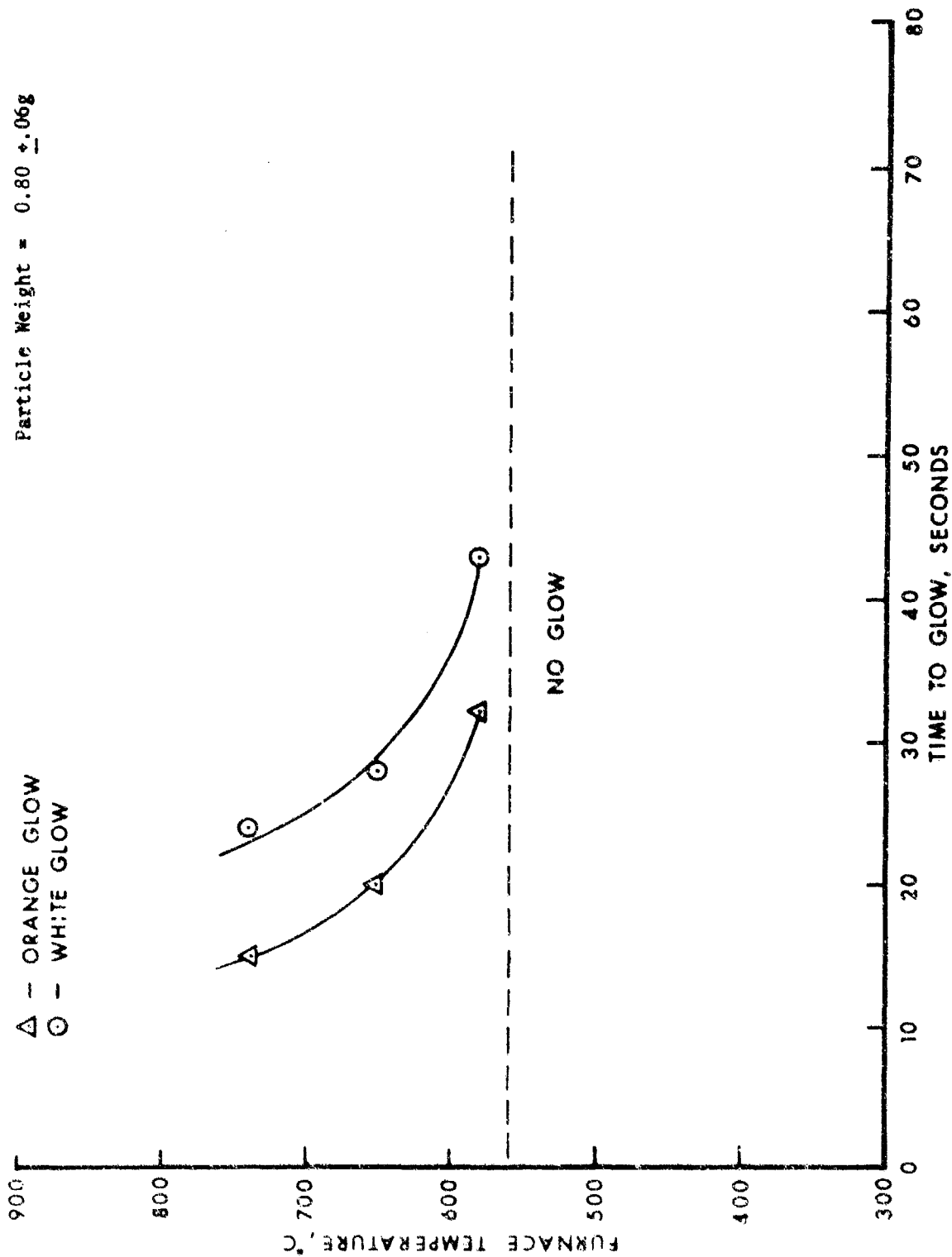


Figure 5 — Effect of Temperature on Zirconium Glow Time

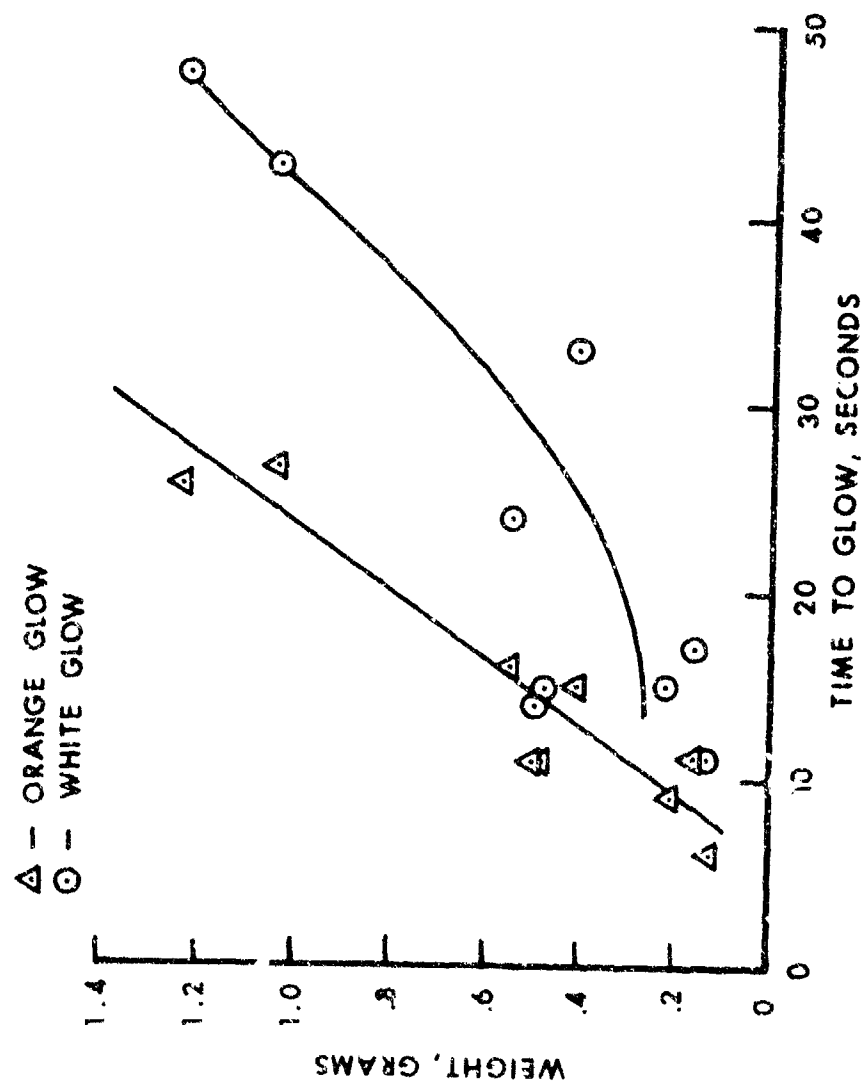


Figure 6 - Effect of Titanium Weight on Glow Time, 920 °C

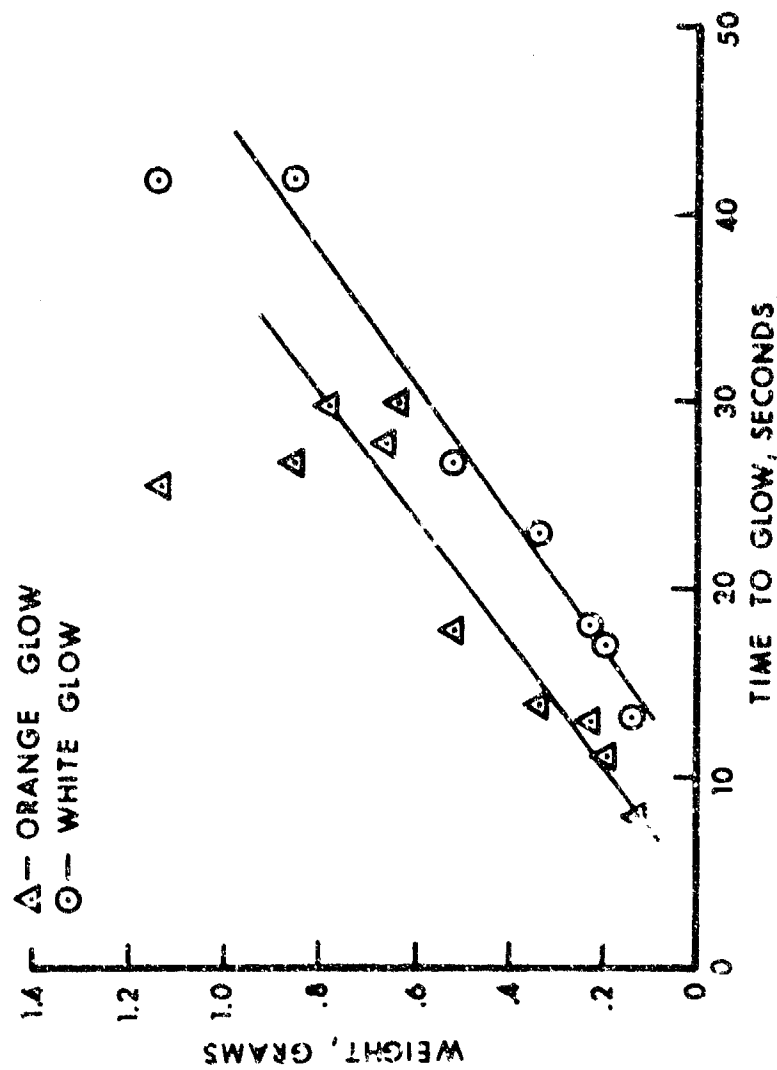


Figure 7 — Effect of Titanium Weight on Glow Time, 970° C

or burn at temperatures up to 900°C.

E. Glow Propagation

The propagation of the glowing was observed with long rods of misch metal. The bright orange glow was observed to propagate down 6" lengths of misch metal rod having a 3/16" diameter. The rods were initially at 22°C and were held horizontal by an asbestos insulated clamp at one end. The other end of the rod was heated intensely by a propane torch. The heated end began to glow with bright orange color and the torch was removed. The glow moved down the 95M rod in air at an average of 2.75 cm/minute leaving a cool, grey, wrinkled rod behind it. The rod gained 4.5% in weight during the glowing. This compares with 25.4% weight gain for complete oxidation as measured after prolonged heating. The rod increased in length by 47% during the heating. The glow would not propagate more than one cm down a similar rod of 75M2 misch metal.

The expansion of misch metal during oxidation can be seen in Figure 8. A rod of 1/16 inch diameter was heated to 650°C in air in a thermal analysis ceramic cup. The cinder-like residue was more than twice the bulk volume of the metal rod.

V. GENERATION OF PYROPHORIC FRAGMENTS

The drop weight impact apparatus that was used to generate pyrophoric sparks and fragments from the glowing samples is shown in Figure 9. The dimensions of the apparatus are shown in Figure 10. The recovered fragments varied in shape and were generally less than 0.1 gram in weight. The sparks were directed at a 45° inclined stainless steel plate which led to an enclosed tray where terminal ballistics experiments were carried out to study fragment properties and ignition of combustible materials. These experiments will be described in later reports.

The order of magnitude of kinetic energy necessary to initiate sparking in the glowing pellets was determined from different drop heights. Photographs of sparks from 10, 20, 30 and 39.1 cm drops are shown in Figure 11.

PELLET
AFTER
OXIDATION

MISCH
METAL
PELLET

DTA
LINER

Figure 8 - Misch Metal Expansion

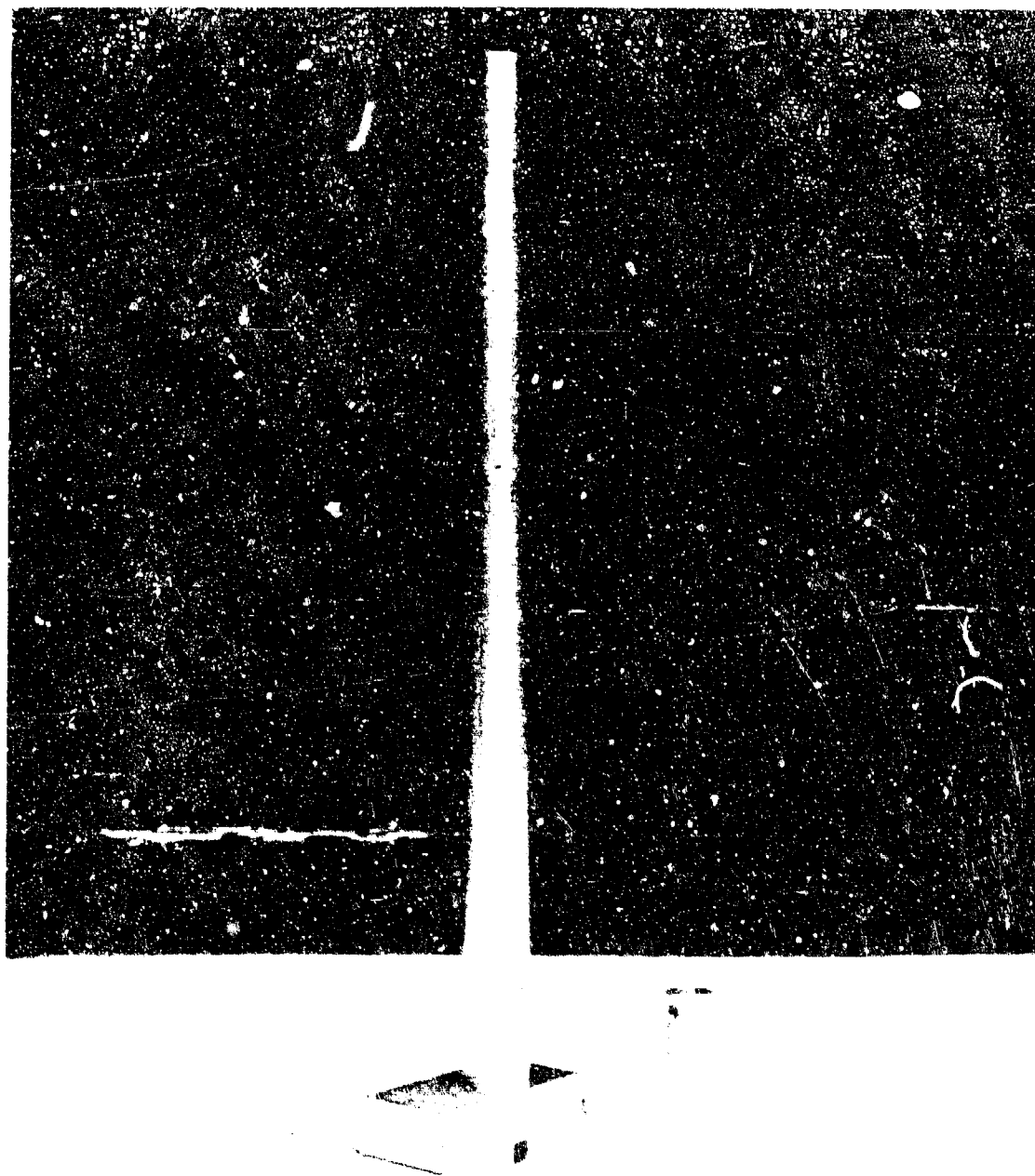


Figure 9 -- Drop Weight Impact Apparatus

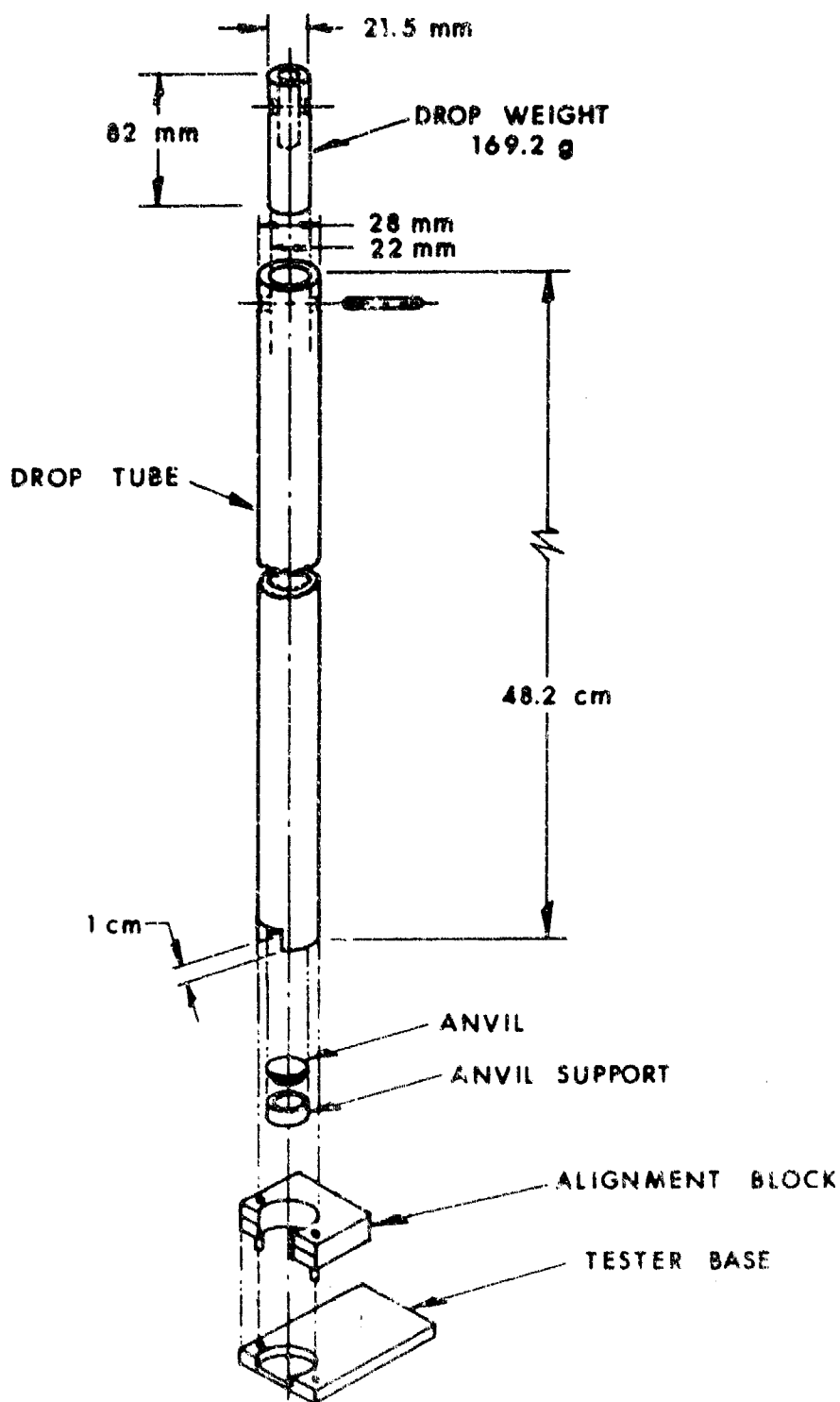
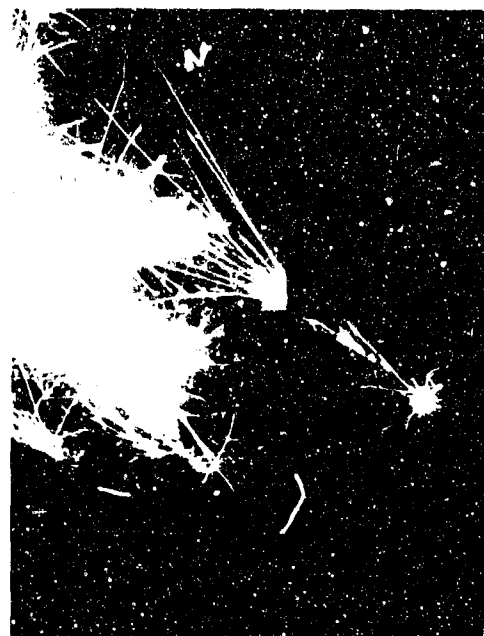


Figure 10 - Drop Weight Impact Apparatus Dimensions



A. 10 cm DROP
(0.166 newton m)



B. 20 cm DROP
(0.332 newton m)



C. 30 cm DROP
(0.498 newton m)



D. 39.1 cm DROP
(0.647 newton m)

Figure 11— Effect of Impact on Spark Formation

These heights correspond to 0.166, 0.332, 0.50 and 0.65 newton meters with a drop weight of 169 grams. Upon falling from a height of 39.1 cm as is the case in most runs, the impact velocity is 276 cm/sec. It seems that a kinetic energy of at least 0.332 newton m is needed for extensive sparking. In some tests glowing pellets were merely dropped from 30 cm. In these tests some sparking occurred, but it was not as dramatic as those generated in the impact apparatus.

High temperatures alone did not cause sparking in the pellets, but the combination of both heat and impact in the ranges discussed here gave profuse sparks. Although either extremely high temperatures ($>1000^{\circ}\text{C}$) or very high kinetic energy impacts alone may lead to sparking, the point to be emphasized is the presence of thresholds of temperature and impact for sparking in the sensitive laboratory conditions described here.

It was shown that an oxidizing atmosphere is necessary to the sparking process by heating a pellet of 75M2 misch metal in air at 700°C . It was glowing brightly when it was placed on the anvil of the impact apparatus which was in a covered tray filled with argon. After impact, small glowing particles dispersed from the impact apparatus, but they were not sparking fragments. They were not bright and cascading. Thus, the misch metal was sufficiently softened at 700°C to easily breakup upon impact. The hot fragments did not "explode" or spark in the inert argon atmosphere.

High speed motion pictures of free flying fragments after impact show an eroding type of breakup of the larger pieces during flight. The fragments had velocities between 1,000 and 2,000 cm/sec.

VI. CONCLUSIONS

A search of the chemical and physical properties of metals revealed that a combination of two properties - the free energy of formation of the metal oxide per oxygen atom and the ratio of metal oxide to metal specific volume - furnished a distinction between known pyrophoric and non-pyrophoric metals. Using these properties, fourteen elements were predicted to possess pyrophoric sparking capability. They have both high reactivity and high oxide volume ratio.

A simple test was developed using heat and impact to experimentally test materials for pyrophoricity. When pyrophoric metals were heated above their Lower Glow Temperature they began to glow brightly and, upon impact with a small standard weight, gave a profuse shower of sparks. The order of Lower Glow Temperature found was (misch metal and cerium) < zirconium < titanium.

Pyrophoric and non-pyrophoric metals were tested as above. The two known pyrophoric metals, cerium and zirconium, sparked vigorously. The two potential pyrophoric metals (according to the above empirical criteria), aluminum and titanium, were tested and while the titanium sparked, the aluminum did not. Three non-pyrophoric metals (iron, copper, and antimony) did not spark.

From these exploratory results it appears that the high reactivity and high oxide expansion criteria are necessary for a metal to be pyrophoric, but are not sufficiently limiting. Additional criteria may be needed to further reduce the field of potential pyrophoric metals.

The thermo-impact bench test can be used to screen new metals and alloys for pyrophoric behavior. It is planned to further study the initiation of pyrophoric behavior and to utilize the sparks generated from the impact as ignition sources in controlled experiments.

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